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EXAFS Analysis of UF₄

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Abstract

As part of our studies of 5f covalency in uranium compounds, we performed a comparative structural study of UF₄ and UO₂, using Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Fine Structure (XANES). This work confirms the quality of our samples and provides additional insight into geometrical issues related to iconicity and covalency.

Discussion

Actinide compounds, particularly actinide dioxides, have a propensity to exhibit covalency in their bonds. [1] Previously, a variety of soft X-ray techniques, including x-ray absorption spectroscopy (XAS) [2], bremsstrahlung isochromat spectroscopy (BIS)[2], resonant inverse photoelectron spectroscopy (RIPES) [3] and X-ray emission spectroscopy (XES) [3,4] have been used to investigate uranium dioxide (UO₂). Now, as a further test of these analytical methods and the interplay of iconicity and covalency in actinide compounds, the studies are being expanded to include uranium tetrafluoride (UF₄). UO₂ and UF₄ are isoelectronic in terms of their formal charge states, i.e. U⁺⁴, and they make an interesting comparison in terms of covalency and iconicity, respectively. However, this comparison is complicated by significant structural differences: UO₂ is in a highly ordered, single site (fluorite) structure [5,6] and UF₄ is monoclinic with two U sites, as shown in Figure 1. [7] It is this structural difference that will be addressed with the EXAFS analysis. Our measurements were made on Beamline 11-2 at the Stanford Synchrotron Light Source. [5]

In the region of the absorption edge, it is possible to observe the large spectral features known as XANES. (Figure 2) For the U L₃ (2p_{1/2}) edge, the threshold is near 17,160 eV. In general, XANES gives a measure of the unoccupied density of states. (8) The UO₂ and UF₄ XANES spectra shown in Figure 1 are similar, with some tantalizing suggestions of differences. The resolution in these measurements, taken in transmission mode, is limited by lifetime broadening and is insufficient to achieve a convincing differentiation. However, measurements made in the RXES (Resonant X-ray Emission Spectroscopy, Ref. 9 and 10) mode do exhibit clear differences, but that will be discussed elsewhere. [11] As the energy of the incoming photons rises substantially above the edge, the spectral features diminish in size and change in nature, becoming the oscillations associated with EXAFS.

EXAFS Analysis of UF₄

EXAFS is a powerful analytical technique for the determination of interatomic distances, with results ranging from water [12] to Pu [13]. The oscillations in the measured fine structure are driven by back-scattering from nearby atoms. While initially measured as a function of energy of the incoming photons, this curve is subsequently converted into a plot of oscillations versus the wave-vector of the outgoing electrons. (Figure 3) Under the best conditions, the analysis can be as simple as a Fourier transform, which generates maxima in the radial distribution functions, associated with rings of nearest neighbors, next nearest neighbors and so on. (Figure 4)

Our EXAFS transform for UO₂ agrees quantitatively with those for UO₂ reported earlier: specifically Figure 2 in Reference 5 and Figure 3 of Reference 6. This leads us to assign the two largest features to the nearest neighbor oxygen atoms ($d = 2.36$ angstroms) and the next nearest neighbor uranium atoms ($d = 3.85$ angstroms), following references 5 and 6. Thus in the UO₂, with its highly ordered (fluorite) structure and single site for U, it is possible to see both nearest neighbor (O) and 2nd nearest neighbor (U) peaks. However, the UF₄ behavior is different: here, only the nearest neighbor backscattering peak is observed. **For UF₄, in a monoclinic structure with two U sites, only the nearest neighbor F ring produces a peak, while the U-U washes out due to the two sites and multiple scattering path distances.**

Acknowledgements

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EXAFS Analysis of UF_4

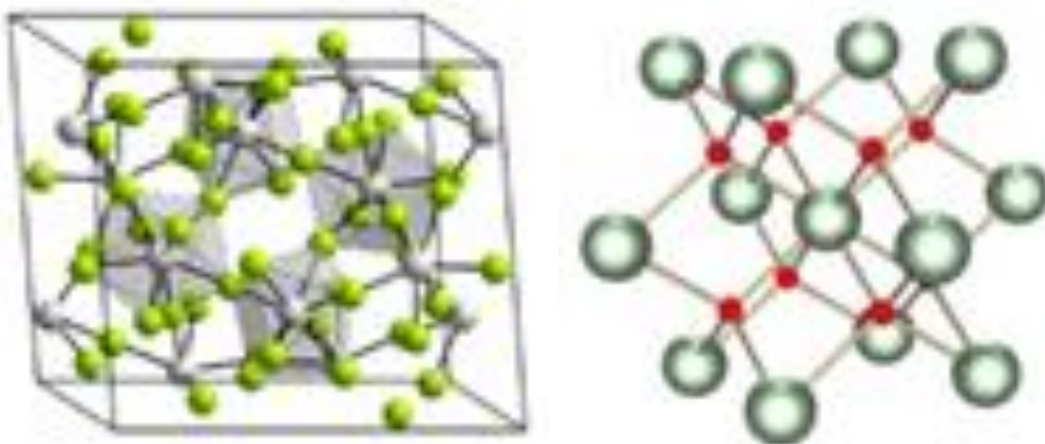


Figure 1 Left: UF_4 is monoclinic, with two types of U; Right: UO_2 is a fluorite (cubic) structure.

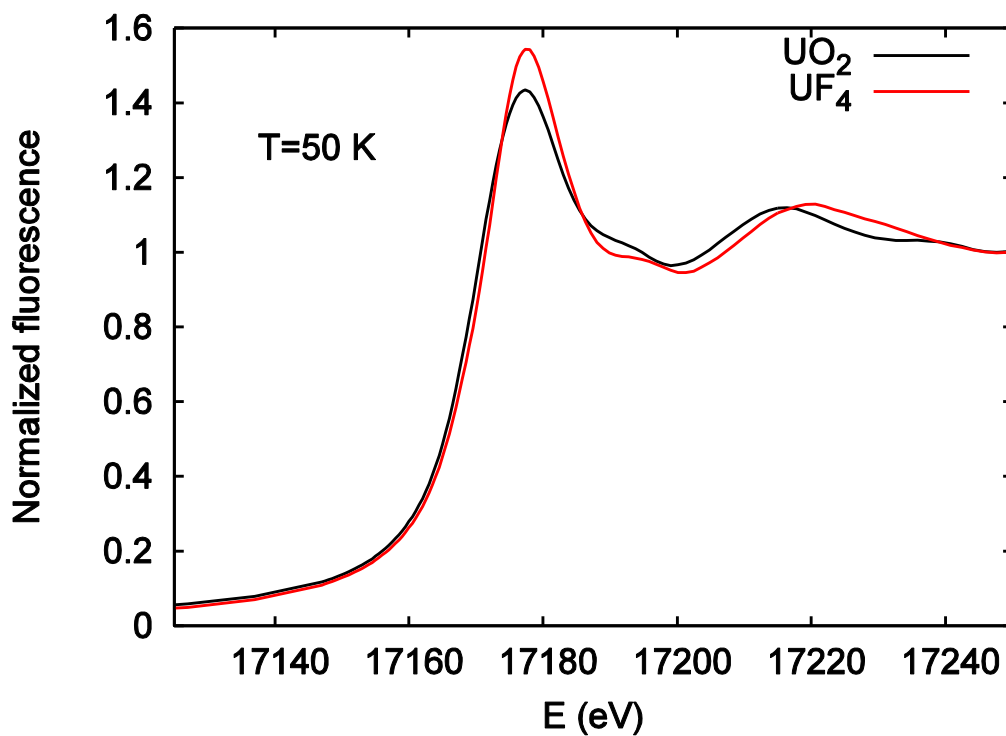


Figure 1 The L3 XANES of uranium dioxide and uranium tetrafluoride.

EXAFS Analysis of UF_4

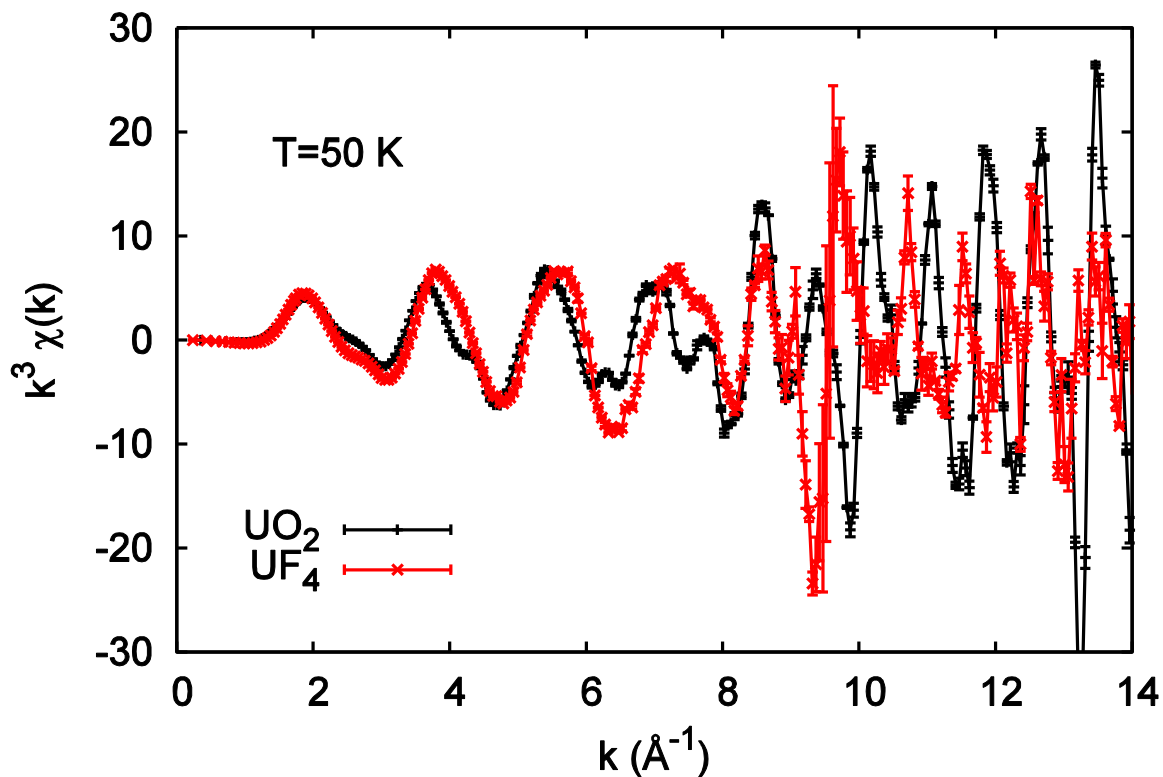


Figure 2 A plot of the EXFS oscillations versus the wave vector of the outgoing electron.

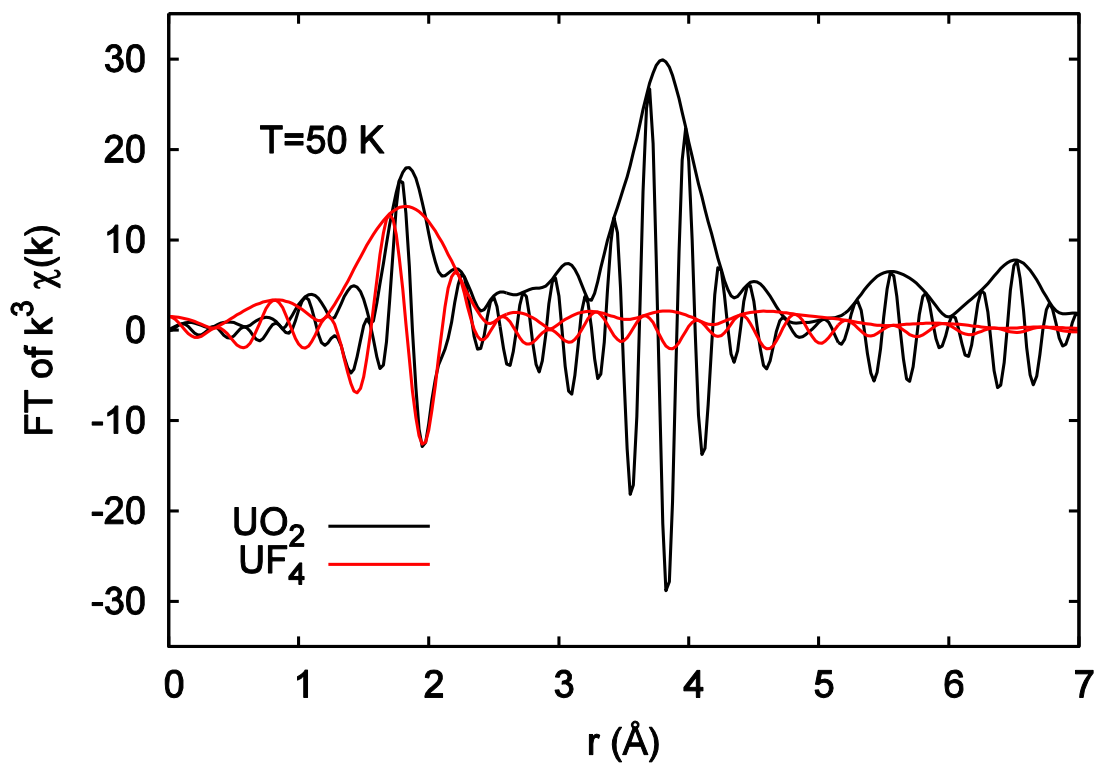


Figure 3 The Fourier Transform of the data in Figure 2.